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Concentration dependence of fading of the open form of 6′-nitroindolinospiropyran in a polymer matrix

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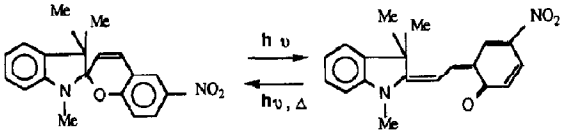
The concentration dependence of the fading process of the open form of 6′-nitroindolinospiropyran (BIPS) in PMMA has been studied by fluorescence lifetime measurements at 77 K. At sufficiently high concentrations, the fluorescence decay becomes bi-exponential which indicates that energy transfer occurs to molecules absorbing at longer wavelengths. This leads to a blue-shift of the absorption maximum during the fading process. The retardation of the decolouration of BIPS with increasing concentration is attributed to the interaction between the permanent dipoles of BIPS. Numerical calculations of the concentration dependence of the decolouration rate, which include the dispersive character of the decay rate due to the polymer matrix, are given.

1. Introduction

The photochromic reaction of 6′-nitroindolinospiropyran (BIPS, **1**) has been extensively studied in the liquid and solid phases and has been employed to study the dynamics of polymer matrices [1,2]. Interest in the phenomenon of photochromism stems from the numerous applications that are foreseen for this effect, for instance, in the field of optical data storage and, on a more mundane level, for use in sun glasses and roofs. The recent finding that the open form of the photochromic spiropyrans can easily form aggregates which exhibit large optical non-linearities has further fuelled interest in these systems [3–5].



1 2

The photocolouration of BIPS is generally accepted to occur after excitation of the closed form **1**, after which the geometry changes to a merocyanine-like form **2**. The absorption of the lowest excited state of the open form is in the wavelength region around 600 nm, and is considerably red-shifted (about 8000 cm^{-1}) relative to the absorption band of the lowest excited state of the closed form. The back reaction of the open, coloured form to the closed form proceeds in solution with first-order kinetics indicating that this reaction proceeds via a well-defined barrier. However, in glasses and plastics like PMMA, the back reaction proceeds on a time scale of minutes to hours and does not obey first-order kinetics [6,7]. This dispersive behaviour of the fading in amorphous systems has been elegantly explained by Richert and Bässler [6,7], who assumed that in amorphous materials a distribution of barrier heights exists for the back reaction.

Two other peculiar aspects of the fading process, namely, an apparent blue-shift of the absorption maximum of the open form during fading and the inverse concentration dependence of the fading process, have been discussed by Eckhardt et al. [8]. These workers showed that under certain conditions, J-aggregates are formed that show a very slow back reaction. The presence of H-aggregates in these polymer matrices was also invoked. By assuming that fading can only occur for those molecules at the end of the aggregate chain, they could account for both anomalous features of the fading process. The problem with this interpretation is, that in many samples

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that show these anomalies, no signature of aggregation is observed.

In this Letter, we report results of fluorescence lifetime measurements on the open form of BIPS in PMMA for various concentrations of the open and closed form. The observation of excitation and detection of wavelength-dependent fluorescence decays at higher BIPS concentrations presents the key result of our experiments. On the basis of this result, we propose a different mechanism for the two aforementioned effects. The blue-shift of the absorption spectrum during fading is attributed to energy transfer among the isomers of the open form. This process leads to a preferential excitation of the energetically lowest merocyanine isomers. Because fading can also be induced by light, energy transfer leads to loss of absorption at the red side of the spectrum.

In order to explain the inverse concentration dependence, we propose an explanation involving static dipole–dipole coupling between the permanent dipoles of BIPS. Numerical calculations, that take account of the dispersive nature of the fading rate, support this idea.

2. Experimental

BIPS was bought commercially. The samples of BIPS in PMMA were prepared as follows: First, a 10 wt.% solution of PMMA in chlorobenzene was prepared. To this solution, different amounts (0.14, 0.5, 1.5, 5 and 15 wt.% BIPS relative to the weight of the polymer) were added. Drops of these solutions were then brought onto different glass plates that were dried in a vacuum desiccator. The films were coloured by UV radiation (366 nm) at room temperature and then cooled down to 77 K in a cryostat. Absorption spectra at 77 K were recorded with a dual-array optical multichannel system (Princeton Instruments). A Schott KG1 filter was used to isolate the relevant spectral output from the tungsten lamp. Fluorescence lifetimes were obtained using equipment described elsewhere [9]. Briefly, a synchronously pumped dye laser, equipped with a cavity dumper, was used for excitation. The repetition rate of the excitation pulses was 100 kHz, the pulse duration 5 ps, and pulse energy 1–10 nJ. The pulse energy incident on the sample was 1–10 pJ, and the beam diameter inside the sample was about 0.2 mm. The emission was detected at right angles using a 0.5 m grating monochromator. The spectral resolution used was about 15 cm^{-1}. The decay of the fluorescence after excitation was time resolved using time-resolved single-photon counting. The instrumental time resolution including the broadening resulting from the grating monochromator was 75 ps. A fluorescence decay was obtained in typically 3–15 min. The emission intensity at 77 K from a freshly excited spot decreased about 5% in a few minutes and remained stable afterwards. No reliable lifetimes could be obtained at room temperature due to efficient bleaching. Fluorescence decay curves were fitted by iterative convolution of the measured system response with a bi-exponential decay function $a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$. Here, a_i, τ_i are free parameters and t the time. Convolutions were calculated in a manner described in ref. [10]; the fitting method (Levenberg–Marquardt) used is described in ref. [11].

3. Results and discussion

In the absorption spectrum at 77 K of an irradiated PMMA film containing 4×10^{-3} M BIPS (0.14 wt.%), three bands at 540, 575 and 635 nm are clearly discernable. The spectrum agrees with spectra published by many other workers [12], who, however, have used much higher concentrations. The result shows that these bands are not concentration dependent, which is an important observation in view of the concentration-dependent blue-shift of this band during fading. We assign these bands to different isomers. The alternative interpretation that these bands are vibronic transitions of the same merocyanine isomer can be ruled out on the basis of the fluorescence-lifetime measurements to be discussed.

For a dilute sample (4×10^{-3} M BIPS), the fluorescence lifetime is found to be 3.4 ± 0.2 ns, independent of excitation and detection wavelength. When the BIPS concentration is raised to 1.4×10^{-2} M (0.5 wt.%) and the sample coloured to an optical density of about 0.5, the fluorescence decays become dependent on both the excitation and detection wavelengths. The most striking feature is the observation of bi-exponential decay if excitation is in the

range 545–580 nm *and* detection occurs in the wavelength region 610–630 nm (see fig. 1). For detection wavelengths above 640 nm, the emission intensity shows a build-up. Disregarding the first 100 ps of the fluorescence decay in this wavelength region, the fluorescence decay is found to be single exponential. The lifetime (3.4 ns) is, within experimental error, equal to the single-molecule lifetime. The results obtained do not depend on the initial concentration of uncoloured BIPS, but mainly on the concentration of the open form. Thus, 0.5, 5 and 15 wt.% samples coloured to an optical density of about 0.5 give nearly identical results. However, if the concentration of the open form is increased, by colouring 0.5, 5 and 15 wt.% samples to the maximum extent possible, the fluorescence decays are found to be very dependent on the concentration of the open form. The decay curves of the 5 and 15 wt.% samples (coloured to the maximum extent possible) could not be fitted satisfactorily with a bi-exponential function, but instead a tri-exponential decay function was found to be necessary. In order to depict a trend as a function of concentration, the experimental data were still fitted using a bi-exponential decay function. It is found that the fast component becomes shorter and acquires a dominant weight factor for increasing concentration. A few examples of decays observed are shown in fig. 2.

The above results can be consistently interpreted by assuming that for the more concentrated samples,

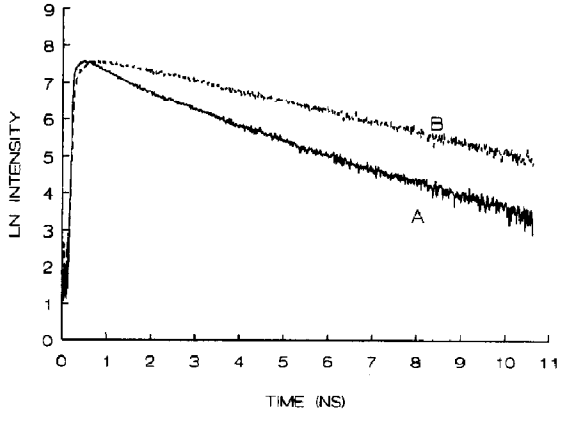

Fig. 1. Fluorescence decay curves of 0.5 wt.% BIPS sample upon excitation at 560 nm: (A) emission detected at 625 nm; (B) emission detected at 650 nm.

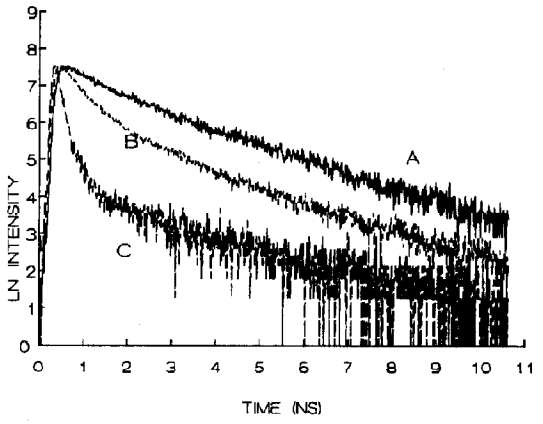

Fig. 2. The dependence of the fluorescence decay on the concentration of the open form of BIPS by colouring (A) 0.5 wt.%, (B) 5 wt.%, (C) 15 wt.% samples, to the maximum extent we could achieve. Excitation took place at 545 nm and the emission was detected at 630 nm.

a Förster-type [13] energy transfer occurs from the isomers absorbing in the wavelength region 545–580 nm to the isomers absorbing at 575 and 635 nm. In particular, the rather restricted region in which bi-exponential decay occurs, the dependence on the concentration, and the growth of the emission in the long-wavelength region strongly point towards energy transfer. Excitation transfer also satisfactorily explains the blue-shift which occurs upon optical pumping of the open form [8]. If one recalls that the decolouration of the open form increases linearly in intensity (see, for instance, ref. [7]), it is obvious that excitation transfer to the isomers absorbing in the long-wavelength region will result in enhanced decolouration at the red side. At the same time, decolouration at the blue side will be quenched, resulting in an apparent blue-shift of the absorption profile. It should be noted that this light-induced decolouration is superimposed on the normal thermally induced fading of the open form.

We now address the question of how to explain the peculiar observation that the thermal-fading rate constant is inversely proportional to the BIPS concentration. We suggest that this fact is due to an increase of the width of the Gaussian distribution of barrier heights caused by static dipole–dipole coupling between randomly oriented BIPS molecules in the open and/or closed form. Both forms possess an appreciable dipole moment [14,15] which, in our

calculations, we assume to be 5 D for both species. While the dipolar coupling averaged over all sites is zero, for an individual molecule the interaction energy may be large, especially at high BIPS concentrations. Results of a calculation of the dipolar energy [#1] as a function of site label b for two different concentrations are given in fig. 3. Note that the rms energy fluctuation increases from a few tenths of a wavenumber at 10^{-3} M ($\approx$0.03 wt.%) to about 50 cm^{-1} at 10^{-1} M. Dipolar coupling thus leads to an additional broadening of the barrier-height distribution that determines the dynamics of the back reaction. Richert [7] has shown that the dispersive nature of the thermal decay of the open form can be calculated using the following expression:

[#1] An expression for the dipolar energy is given in the textbook mentioned in ref. [16].

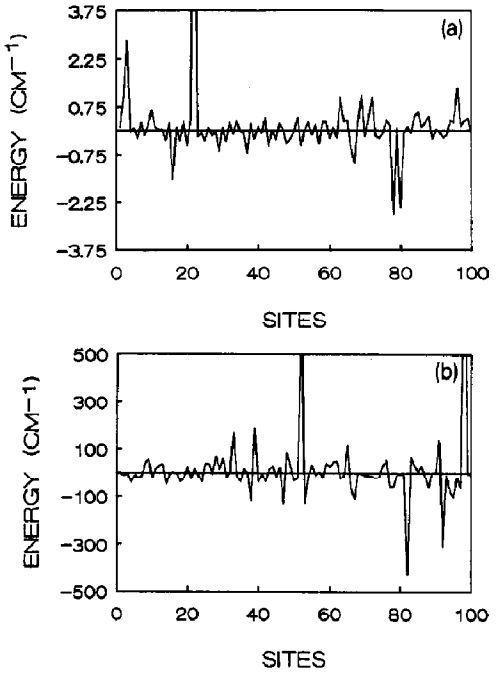

Fig. 3. Illustration of the variation of the dipolar energy over 100 different sites. Energy (in cm^{-1}) is calculated, assuming randomly distributed and oriented dipoles of 5 D (1.66×10^{-29} cm). (a): concentration of the dipoles 10^{-3} M. (b): concentration of the dipoles 10^{-1} M. Note that the fluctuations in energy increase about 100 times if the concentration is also increased by a factor of 100.

$$M_0(t)=\frac{1}{\hat{\sigma}^{\mathrm{app}}\sqrt{2\pi}}\int_{-\infty}^{+\infty}\mathrm{d}\epsilon\exp\left(-\frac{\epsilon^2}{2(\hat{\sigma}_{\mathrm{app}})^2}\right)\times\exp(-\nu^{\mathrm{app}}te^{-\epsilon}), \quad (1)$$

where $M_0(t)$ is the decay of the open form, $\hat{\sigma}^{\mathrm{app}}\equiv\sigma^{\mathrm{app}}/kT$ is the width of the Gaussian distribution of barrier heights due to the inhomogeneous free-volume distribution in the polymer, ν^{app} the fading-rate constant of sites positioned at the center of the Gaussian density of activation energies ϵ. In a PMMA matrix, $\hat{\sigma}^{\mathrm{app}}$ is known to be 1.25 ± 0.1 [7]. We assume that, due to dipolar coupling, the width σ^{app} of the probability distribution of ϵ becomes

$$\hat{\sigma}^{\mathrm{app}}=\hat{\sigma}_1^{\mathrm{app}}+\hat{\sigma}_0^{\mathrm{app}}, \quad (2)$$

where $\hat{\sigma}_1^{\mathrm{app}}\equiv\sigma_1^{\mathrm{app}}/kT$ is due to dipolar coupling, and $\hat{\sigma}_0^{\mathrm{app}}=1.25$, the width at infinitely low concentration. Note that ν^{app}, being defined at the centre of the distribution of activation energies, is not changed as the mean value of the dipolar interaction is zero. Using the numerical result for the dipolar energy (see fig. 3), we have, in the case of a concentration of 10^{-1} M, $\sigma_1^{\mathrm{app}}\approx50$ cm^{-1}. Fig. 4 shows the results of a calculation of $M_0(t)$ at 300 K for a very dilute sample and at a concentration of 0.1 M. The slowing-down of the fading process at higher concentrations is very clear, showing that dipolar interaction among the photochromic molecules has an effect on the fading process. A quantitative analysis of the concentration dependence of the fading is very complicated, because also the effect of energy transfer has to be taken into account. We suggest that oxazines [17] are more suitable for a study of the effect of dipolar interaction on fading. In the case of oxazines, the open form seems to exist in only one isomer [17]. In addition, we found the fluorescence of the open form to be extremely weak. These two properties of the open form of oxazine strongly suppress the effects of energy transfer on fading, leaving only the effect of dipolar interaction.

Summarizing, we have shown that the fading process in the photochromic reaction of BIPS is complicated by energy transfer among isomers of the open form, and that static dipolar coupling has a dramatic effect on the concentration dependence of the back reaction. These findings are not only interesting in

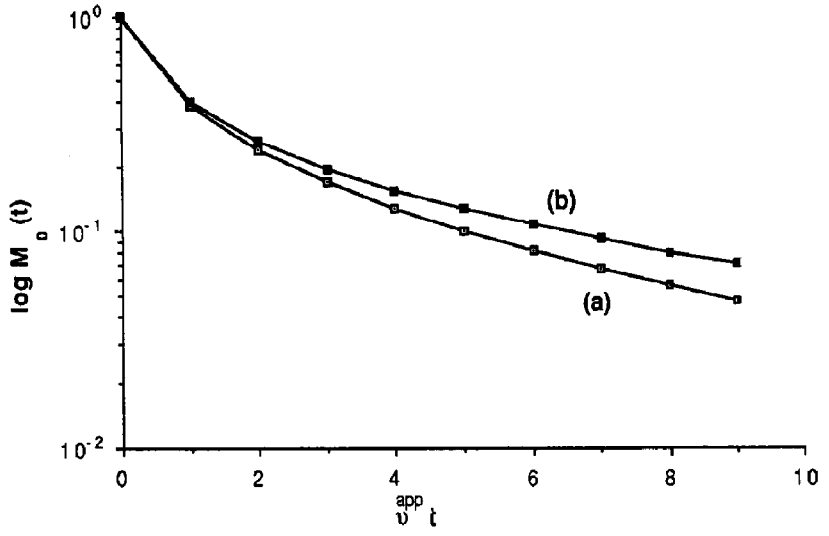

Fig. 4. Thermal fading at $T=300$ K of the open form calculated from eq. (1). Curve (a), calculated with $\hat{\sigma}^{app}=1.25$ (from ref. [7]), corresponds to infinitely low concentration of spiropyran. Curve (b), calculated with $\hat{\sigma}^{app}=1.50$, corresponds to a concentration of about 10^{-1} M, as discussed in the text.

themselves but are also relevant to applications of photochromic materials.

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